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IMMISCIBLE LIQUIDS AND VAPOURS IN SOIL: RECENT EXPERIMENTS ON TRANSPORT AND CONTROL

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ABSTRACT

This paper provides a summary of some recent results from an on-going research programme studying the transport and control of hazardous immiscible liquids and their vapours in soil environments. Results are presented on the transport of pentane vapours from two different liquid source configurations within a long, thin chamber containing dry sand. The results were then successfully simulated using a two-dimensional mathematical mass transport model and these simulations are shown graphically. The paper also provides preliminary results from laboratory scale experiments examining air venting as a means of removing volatile solvents from soil. One such experiment involves an air purge of 50 cm of sand with the lower quarter of the column containing hexane at residual saturation. The results show an increase in hexane content of the exhaust gas to near ambient vapour pressure and then a decrease as the liquid in the soil reaches depletion. A mass balance showed a nearly complete recovery of the hexane. Subsequent experiments have studied the impact of air flow rate, source geometry and air flow configuration on recovery efficiency. Experimental work has also been done to examine vapour adsorption on soil and recent results are presented.

INTRODUCTION

This paper presents some recent results of studies on the behavior of immiscible liquids and their vapours in soil. This is part of a research programme that has been underway for the past four and one-half years at the University of Waterloo in the Department of Civil Engineering. The work has been jointly supported by the Ontario Ministry of the Environment (Project No. 334PL) and the Natural Sciences and Engineering Research Council (NSERC).

While both liquid and vapour behavior are being examined as a part of the research programme, this paper deals primarily with recent vapour investigations. Three distinct topics are addressed.

1. Testing the suitability of a previously developed vapour transport model to simulate laboratory experimental results on hazardous vapour movement in soil.

2. The design and use of experiments to study the adsorption of vapours onto soil.

3. Experiments to investigate the parameters which affect the design and performance of forced air venting systems to remove volatile organic solvents from soil.

The equipment and experimental results for topic 1. have been described previously (Farquhar et al., 1987). The model simulations and all of the information presented on topics 2. and 3. have however not been presented prior to this.

SIMULATION OF EXPERIMENTS ON VAPOUR TRANSPORT IN SOIL

Two types of experiments were completed in the study of vapour transport through soil; one involving a vertical column of soil, 7.0 cm in diameter and 36.0 cm long and the other using a rectangular flux chamber, 3.7 m long, 1.2 m high and 0.15 m wide. These pieces of equipment, shown in Figures 1 and 2 respectively, and their operation have been described in detail elsewhere (Farquhar, et al., 1987) and only a brief summary is given here. It was possible with the column to add a vapour source to either the top (headspace) or the bottom (footspace) of the column and then to observe its movement through the soil sample by means of vapour extraction at the sampling ports. Pressure measurements across the soil column were also taken. Soils included dry sands (moisture content < 1% w/w) and methane as a gas and pentane, hexane and acetone as vapours from liquid sources were used. The duration of the experiments ranged up to 95 hours.

The same soils and vapours were also used in the rectangular flux chamber. It was possible to introduce vapours at the base of the chamber to simulate vapour movement away from a pool of solvent perhaps lying on the zone of saturation. The apparatus for generating a bottom vapour source consisted of a prismatically shaped tray in which variable liquid surface areas could be maintained. Vapours moved upward from the tray through a stainless steel screen and into the soil. A second device was used to simulate a liquid vapour source suspended above the zone of saturation. This involved an external flask containing liquid connected to a perforated teflon tube inside the chamber. Vapour produced in the flask moved through the pipe and into the chamber. Vapour transport throughout the chamber was detected with the use of syringes inserted at the sampling ports shown on Figure 2. Gas chromatography served to quantify vapour concentrations in the samples collected.

The data collection programme encompassed over 30 experiments in which vapour transport away from the source was measured. Transport model simulations were performed on several of these and samples of these simulations comprise a part of this paper.

1. The Vapour Transport Model

The vapour transport model (AD2D) used in these simulations is an adaptation of an earlier model developed as a part of this research programme (Allan et al., 1985). The model solves equations for fluid flow through porous media in two dimensions based on the principles established by Bear (1972) with vapour concentrations expressed on a molar basis. Density driven flow resulting from body forces, diffusion as well as pressure gradient flow, variability in soil type and soil moisture content and reactions between soil and vapour are all features which have been incorporated into the model. Either concentration specified (Dirichlet) or flux specified (Cauchy) conditions can be specified at the soil boundaries. Solution to the partial differential equations is achieved through the use of finite element methods and, in particular, the Galerkin Method of Weighted Residuals.

The original model was adjusted by Kell (1988) for execution on a personal computer (IBM PC compatible) with 360 k memory. It was revised to accommodate transient pressure distributions to account for density dependent flow and was used in this form for all simulations.

2. Simulation of Experiment Results

The data on soil and vapour properties used in the simulations are summarized in Table 1. Finite element size and shape and time steps used are described elsewhere (Kell, 1988).

2.1 Column Experiment Simulation

The information in Figure 3 involves the downward transport of acetone vapours through a vertical column of sand from a liquid source in the headspace. The average acetone vapour concentration at the source (C_o) was 15.1% v/v. The upper portion of the figure shows actual data collected at the sampling ports after 25, 45, 100 and 200 minutes. The nonlinear shapes of the curves are consistent with transport induced by both diffusion and density driven flow. The density of acetone is greater than that of air and thus a downward force was operative. Diffusion only, as seen with the experiments on the downward transport of methane (lighter than air), produced linear relationships on similar plots (Farquhar, et al., 1987).

The lower portion of the curve shows AD2D model simulations of the actual data measured at 200 minutes. The simulation with only diffusion and body force induced transport with Dirichlet boundaries at both the top and bottom of the column did not fit the data well. The fit was improved with the inclusion of a source pressure (ΔP) = 5.0 Pa (pressure gradient of 13.3 $Pa.m^{-1}$). This is a very small pressure gradient and not detectable with the manometers in use at the time of experimentation. Although the source headspace was open to the atmosphere through 2-10 cm orifices, some pressure buildup due to acetone volatilization could be expected. More recent experiments using a pressure transducer did detect small pressure accumulations in the range from 5 to 10 Pa.

A sampling port located at the bottom of the column between the sand and the supporting screen yielded acetone vapour concentrations on the order of 1% v/v as opposed to the 0% v/v concentration Dirichlet boundary condition assumed in the simulation. Thus a Cauchy flux boundary appeared to exist at this outlet point of the column. Although the AD2D model can accept a Cauchy flux boundary at the outlet, there were no means available at the time to quantify this flux.

Experimental results and their simulation are shown in a similar way on Figure 4 for the upward transport of acetone from a bottom liquid source. Early in the experiment (at 25 and 45 minutes) the nonlinear nature of the transport is quite evident. Because acetone vapour is heavier than air, it is accumulating more in the lower portion of the soil and is moving upward by diffusion and possibly due to a small pressure gradient. As shown in the lower set of curves simulating the vapour position after 200 minutes, the addition of a $\Delta P = 5$ Pa improved the simulations greatly although this pressure head was below the detection limits of the equipment used.

In general, the ability of the model to simulate the one-dimensional column experimental data, given the inconsistencies in the input information noted above, was quite good. This also proved to be the case for other sand column experiments performed using methane and pentane as migrating vapours.

2.2 Two Dimensional Vapour Flux Chamber Experiments

Acetone as a Bottom Vapour Source

The information presented in Figure 5 shows experimental data and transport model simulations for acetone vapour movement in the two-dimensional flux chamber. The acetone source was a pool of liquid located beneath the soil at the midpoint of the chamber bottom. The sides and ends of the chamber were sealed while the top of the soil was open to allow vapour discharge. The data are presented as vapour concentrations in air as % v/v emanating upward from the 7% v/v vapour source. The concentration contours were found to be symmetrical about the centreline of the box and thus only one-half of the contours are shown from the source to one end of the chamber.

The upper figure presents the experimental data at 95 hours and demonstrates that the acetone vapours had moved upward and outward from the source toward the open top surface. Concentration contours range from 0.5 to 2.5% v/v and have shapes that are consistent with diffusional transport. The low slopes of the contours imply lateral movement due to body forces acting on a heavier vapour. No pressure build-up was detected at the source as the vapour moved outward into the air filled soil pores.

The lower figure shows the transport model simulations after 95 hours of experiment time. The simulated vapour concentration contours have the proper shape but tend to exceed the measured data at all concentrations. The simulations were carried out with Dirichlet boundary at the source and a Cauchy boundary using a radiation condition at the open surface. All input parameters were measured or estimated and no curve fitting was done. As a consequence, the transport model simulations were thought to be reasonably good.

Pentane as a Bottom Source

Experiments identical to those using liquid acetone as a bottom vapour source were performed with liquid pentane. Examples of the experimental results obtained are presented in Figures 6 and 7 for 24 and 72 hours of transport respectively. The upper portions of Figures 6 and 7 show the experimental data collected as concentration (% v/v) contours. The progress of the heavier pentane vapours moving through the previously air-filled soil pores is shown by comparing the two figures. From 24 to 72 hours, the contours have moved laterally and upward from the 18% v/v vapour source toward the open surface consistent with the diffusion of a heavier vapour. Lateral migration is shown to have occurred toward the sealed boundary at the left edge of the graph. Extensive lateral migration would be expected under certain field conditions.

The simulations performed at the two times are shown in the lower portion of the figures and are seen to be excellent. Once again, the simulations were performed with measured or estimated data and no curve fitting to the experimental data was performed. The transport model was judged to function extremely well in this case.

Pentane as a Suspended Source

The 2-D flux chamber was also used to simulate field situations where solvents have been spilled and remain as interstitial fluid within the vadose zone. This can then serve as a source for subsequent vapour transport. To accomplish this, a source of pentane vapour (11% v/v) was introduced at the centreline of the chamber and 0.75 m above the bottom. The movement of vapours away from the source was then tracked and is represented in Figures 8 and 9 for 12 and 72 hours respectively. The vapours are shown to have moved outward radially from the source with increased transport down and then outward. This is consistent with the diffusional together with the body force driven flow of a heavier-than-air vapour such as pentane. The progress of the vapours is seen through comparisons of the two figures. The vapours are being vented at the open top surface and excluded at the sealed left-hand boundary. The results confirm that such situations in the field could produce vapours at depths much greater than the actual spill location. These vapours could, in turn, then contaminate the groundwater through dissolution.

The transport model simulations performed for the two times are shown in the lower portions of the figures. These are seen to be excellent without the aid of curve fitting.

2.3 Comment

The experiments performed, a sample of which have been presented here, have demonstrated some important trends in vapour transport in soil. In particular, these relate to the relative impact of diffusional flow along concentration gradients, advective flow along pressure gradients and vertical flow due to body forces. The results are of value in spite of the specialized conditions of the work such as laboratory scale, single soil types, low soil moisture contents and single vapours.

The research has also shown that the 2-D vapour transport model, AD2D, is capable of producing excellent simulations of experimental

results. The success of the simulations appear to be more dependent on the quality of the input information than on the model and its structure.

EXPERIMENTS TO ESTIMATE THE ADSORPTION OF VAPOURS ONTO SOIL

Part of this research effort was committed to developing methods and then using them to quantify the adsorption of vapours onto soil. The transport model AD2D has the capability of including vapour adsorption during transport but little data were available at the time of the study to allow inclusion of this process.

A method was developed based on the work of Thibodeaux (1984) and used for several adsorption experiments involving three soils, a clay, a well-graded sand and a poorly-graded Ottawa sand and several vapours including pentane, acetone and trichloroethylene (TCE).

The apparatus used and shown in Figure 10 consisted of a 21.4 L sealed glass dessicator fitted with a pressure release valve connected to a water seal. Samples of soil were added to 30 ml jars and the jars plus soil were then weighed and placed into the dessicator. Various volumes of liquid contaminant were placed in the bottom of the dessicator and the top of the dessicator was then sealed in place. The vapour concentration produced depended upon the volume of liquid added as did the pressure build-up in the dessicator. The vapour was allowed to be in contact with the soil for 24 hours and the residual vapour concentration was then determined through extraction at the sampling port. The dessicator was opened and the sample jars then sealed and weighed to determine increased weight due to vapour adsorption. Controls using soil-free jars were run to account for adsorption onto the glass. Tests were performed to quantify the time needed for equilibrium to be reached, the effect of mixing the soil and the extent of desorption under atmospheric conditions.

The results of the work were expressed as adsorption isotherms; mass of contaminant adsorbed (q) in g of contaminant per 100 g soil plotted against equilibrium vapour phase concentration (c) in % v/v. An example of the results obtained is found in Figure 11 showing Freundlich isotherms for acetone adsorbed onto sand (0.9% H_2O w/w) and clay (0.1% H_2O w/w). The saturated acetone vapour concentration in air was estimated to be approximately 26% v/v at the average experimental temperature of approximately 22° C.

The data in Figure 11 show that much more acetone was adsorbed onto the clay soil than onto the sand. The data follow the Feundlich form until a vapour concentration of approximately 18% V/V or about 70% of the vapour saturation in air. At this point, the apparent adsorption increased dramatically and this was found to be the case in all of the experiments run. The reason for this substantial increase is not known but it was speculated that vapour condensation was beginning to occur on the soil and that this, in turn, made it seem that the mass adsorbed was increasing.

Since the soils were extremely dry, the contaminant removal in the Freundlich section of the curve was attributed to adsorption, the dissolution into pore water having been eliminated.

Similar results were obtained for other volatile chemicals and those for TCE are shown in Figure 12.

The results obtained from these experiments showed that adsorption of the chemicals used in the vapour transport experiments through sand was negligible. The adsorption component of the AD2D transport model was therefore not used in the simulations discussed in the previous section. Adsorption onto clay soils was however more significant and thus, the isotherms produced will be of use in simulations involving these soils.

Further studies will be performed with wet soils and the results compared to those of the current investigation. The separate quantification of dissolution and adsorption should be possible.

EXPERIMENTS ON THE USE OF FORCED AIR VENTING TO REMOVE VOLATILE ORGANICS FROM SOIL

Forced air venting is an important means for the removal of volatile organic liquids from soil either within the vadose zone or as a pool on top of the zone of saturation. There are frequent references in the literature to the use of forced air venting the field but little information is available on the fundamental processes involved;

1. The range of air flow rates possible.
2. The effect of spill shape and geometry on recovery efficiency.
3. The impact of soil type, stratification and moisture content on recovery efficiency.
4. The extent of contaminant recovery possible.

As a result, this laboratory scale research project was undertaken to examine some of these fundamental concerns and to assist the predictability of system performance. The work is still in progress but some preliminary results are available and these are presented subsequently. The work plan calls for the following experimental components:

1. One-dimensional columns and 2-D flux chamber experiments with equipment similar to that used in the vapour transport work.
2. Varying sizes and shapes of "spills".
3. Air flux rates ranging up to 4 $L.cm^{-2}.\ hr^{-1}$.
4. Soils ranging from coarse sand to sandy silt.
5. Soil moisture contents ranging from dry (1% H_2 w/w) to field capacity.
6. Two chemicals, hexane and TCE.

To this point in the research, several experiments have been performed using a 1-D column (60 cm long, 10 cm diameter), dry sand (K = 10^{-2} $cm.s^{-1}$) and hexane. Two rotometers one on the air intake and the other on the exhaust gas stream were used to measure gas flow rates while a pressure transducer detected pressure differences across the

soil column. Two different methods were used to introduce hexane into the column.

1. Hexane Residual in Soil at the Column Base

Hexane was introduced into the bottom of the sand column to a height of approximately 14 cm and then allowed to drain leaving a residual of liquid within the soil. The column had been weighed previously and was then weighed subsequently to determine the amount of hexane remaining in the soil. An air flow rate of 1.32 $L.cm^{-2}.\ hr^{-1}$ was introduced into the base of the column and the exhaust gas flow rate and hexane concentrations were measured. The data presented in Figure 13 were collected and show that the saturated concentration of hexane vapour in air (19% v/v) was reached in the exhaust gas in about 30 minutes. It remained at that value until approximately 60 minutes at which time the concentration reduced quickly to near zero. Subsequent weighing confirmed that nearly 100% of the hexane had been recovered.

Because of the vapourization of liquid hexane, the exhaust gas flow rate was significantly greater than the inlet air flow rate. The pressure drop across the column reduced from approximately 1.5 kPa at the start to 1.3 kPa at the end due likely to the increased gas conductivity as the liquid hexane was removed from the soil pores.

In a subsequent experiment, the air flow rate was reduced by one-half to 0.66 $L.cm^{-2}.\ hr^{-1}$. The exhaust gas vapour concentration reached saturation at about the same time but remained there for twice as long as the previous experiment and then dropped to zero abruptly.

The trend observed in this experiment where the exhaust vapour concentration builds up to saturation and stays there until depletion, is consistent with expectations in the design of field systems. In these experiments all the air supplied passed through the zone of contamination. In many field cases, however, it is likely that a substantial portion of the induced air flow will by-pass the zone of contamination. In these cases, it is therefore not possible to predict the exhaust gas vapour concentration, the time required to vent the zone and the recovery efficiency.

2. Hexane Residual as a Cylindrical Slug Within the Soil

In these experiments, hexane was introduced into the column through a smaller diameter brass tube and allowed to drain creating a cylindrical slug of hexane with the soil. The cylinder was weighed to determine the mass of hexane remaining. Forced air was then passed upward through the column in a direction along the axis of the slug (and the column). Inlet and outlet gas flow rates and pressure differentials across the column were measured.

The results of five experiments are shown in Figures 14 and 15. The mass of hexane in the experiments was 20, 30 or 40 g and the inlet air flow rate was 0.75 or 1.5 $L.cm^{-2}.\ hr^{-1}$. In these experiments, the total inlet air flow did not pass through the zone of contamination and, as was expected, the exhaust gas was not saturated with hexane.

The data in Figure 14 also show that the exhaust gas concentration depends on both the mass of hexane present in the soil and the air flux rate. The highest concentrations occurred with the highest initial liquid hexane concentration (40 g) and the lowest air flux rate (0.75 $L.cm^{-2}.\ hr^{-1}$). Conversely, the lowest concentration occurred with the lowest initial liquid hexane concentration (30 g) and the highest air flux rate (1.50 $L.cm^{-2}.\ hr^{-1}$). However, the time required to strip the hexane completely reduced with increased air flux rate.

Figure 15 shows that the rate of hexane removal increased with increased air flux rate and was independent of initial hexane concentration at the 30 and 40 g levels. At the 20 g initial hexane level but at an equivalent air flux rate, the rate of hexane removal became dependent upon the initial hexane level.

In all experiments, in excess of 95% recovery of hexane was experienced.

3. Comment

The results of the forced air venting experiments are only preliminary but certain important trends are evident at this time. The most important is that the assumption of saturated vapour concentrations in the exhaust gas at a site where forced air venting is used is not justified unless all the air passes through the zone of contamination. This is unlikely to be the case in most field applications. The results to date have also shown that the exhaust gas vapour concentration and the time to achieve complete removal depend heavily on the air flow rate, the mass of contaminant spilled and the geometry of the spill. It is anticipated that further experimentation will allow these dependencies to be quantified for use in system design.

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Table 1 Vapour and Soil Parameters Used in Simulations

Viscosities (μ, Pa.S)

Methane	Pentane	Acetone	Air
1.05×10^{-5}	6.7×10^{-6}	7.3×10^{-6}	1.8×10^{-5}

Effective Diffusion Coefficients (D_e, $m.^2\ s^{-1}$)

Methane	Pentane	Acetone
1.7×10^{-5}	7.1×10^{-6}	1.3×10^{-5}

Soil Properties (Uniform Sand)

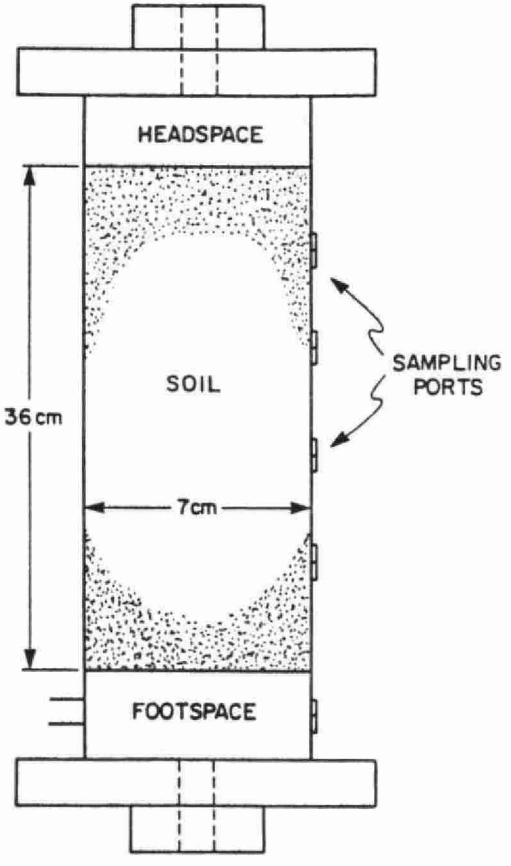
ε (air filled porosity) = 0.35

K_x and K_z (intrinsic permeability) = $1.45 \times 10^{-11}\ m^2$

M (moisture content) < 1% w/w

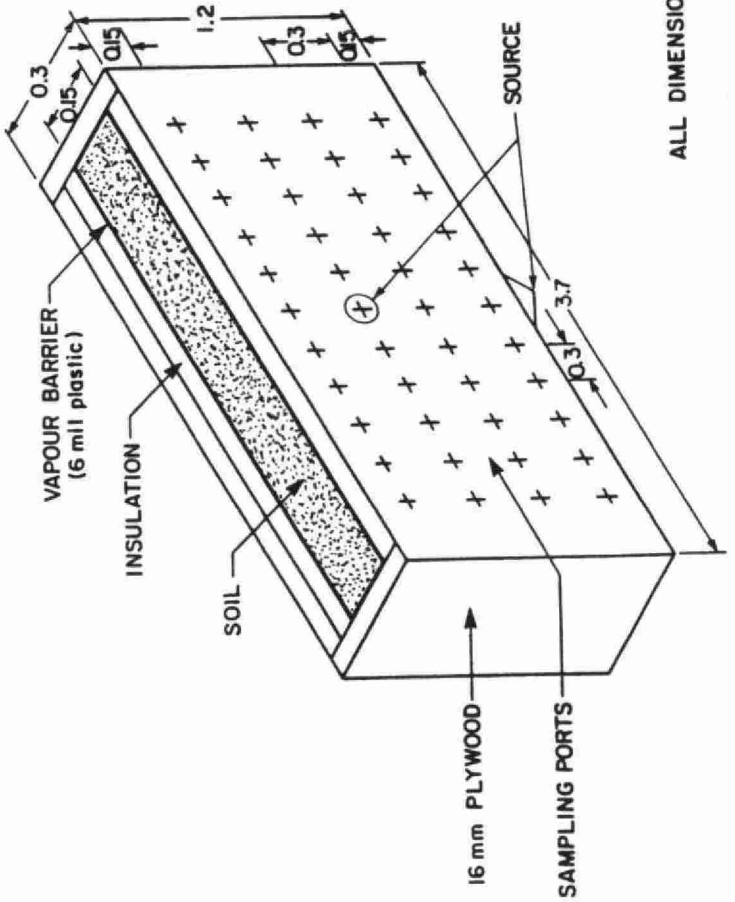
FIGURE CAPTIONS

Figure No.	Caption
1	1-D vapour flux column with source space at the top and bottom
2	2-D vapour flux chamber with source additions at the or suspended in the soil
3	Downward flux of acetone vapours through dry sand: upper, experimental data; lower, simulations
4	Upward flux of acetone vapours through dry sand: upper, experimental data; lower, simulations
5	Acetone vapour flux in 2-D chamber from bottom source after 95 hours: upper, data; lower, simulations
6	Pentane vapour flux in 2-D chamber from bottom source after 24 hours: upper, data; lower, simulations
7	Pentane vapour flux in 2-D chamber from bottom sources after 72 hours: upper, data; lower, simulations
8	Pentane vapour flux in 2-D chamber from suspended source after 12 hours: upper, data; lower, simulations
9	Pentane vapour flux in 2-D chamber from suspended source after 72 hours: upper, data; lower, simulations
10	Apparatus used to measure vapour adsorption onto soil
11	Isotherms for acetone adsorption onto dry clay and sand soils
12	Isotherms for trichloroethylene (TCE) onto dry soils
13	Hexane vapour concentrations in gas exhausted from soil during 1-D forced air venting experiments: source as residual hexane across the base of the soil
14	Hexane vapour concentrations in gas exhausted from soil during 1-D forced air venting experiments: source as residual hexane in a slug within the column
15	Cumulative mass of hexane exhausted from 1-D forced air venting experiments: source as residual hexane in a slug within the column



1-D VAPOUR FLUX COLUMN

Figure 1



2-D VAPOUR FLUX CHAMBER

Figure 2

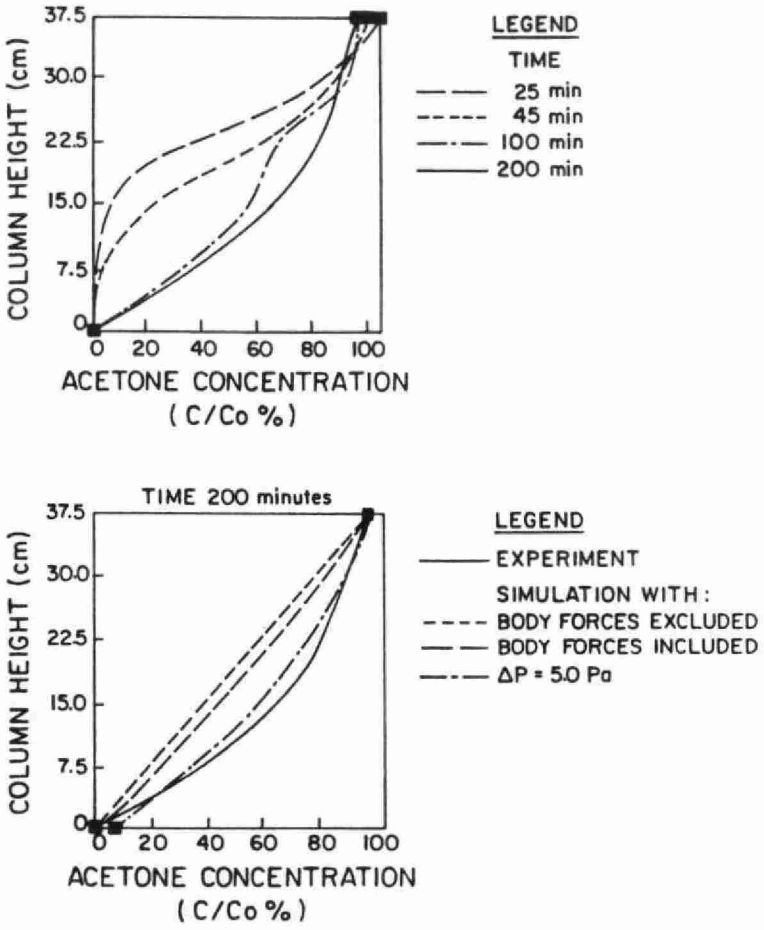


Figure 3

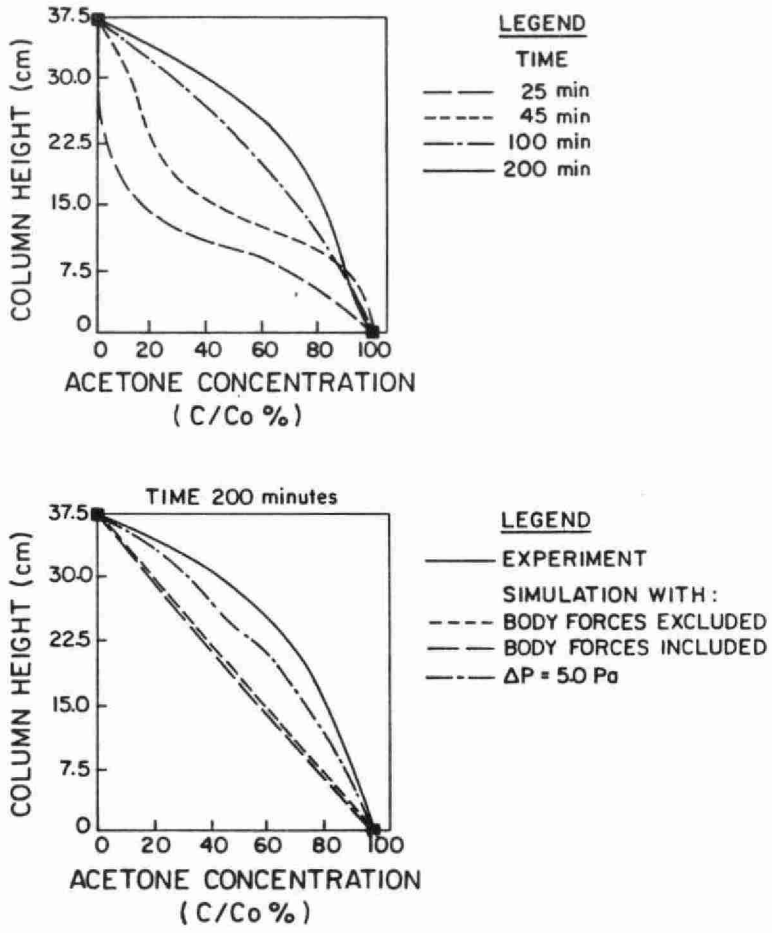
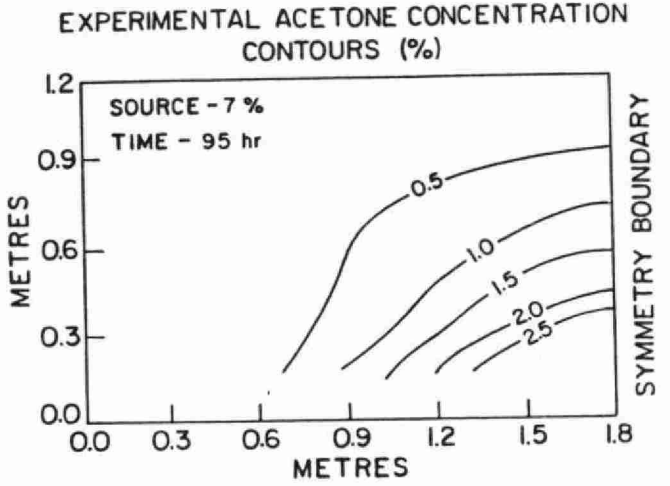


Figure 4



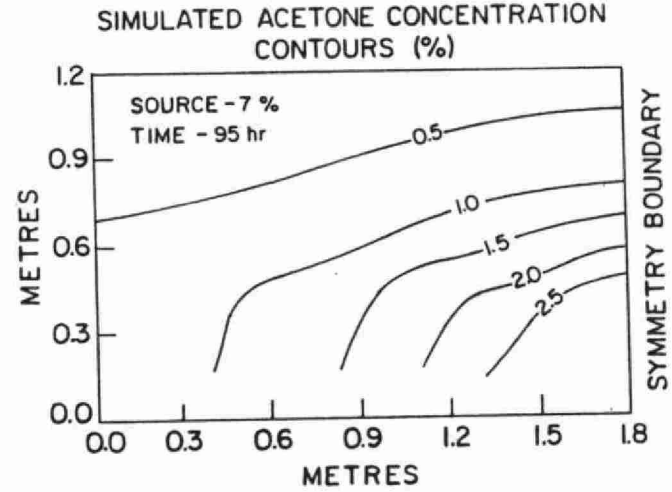
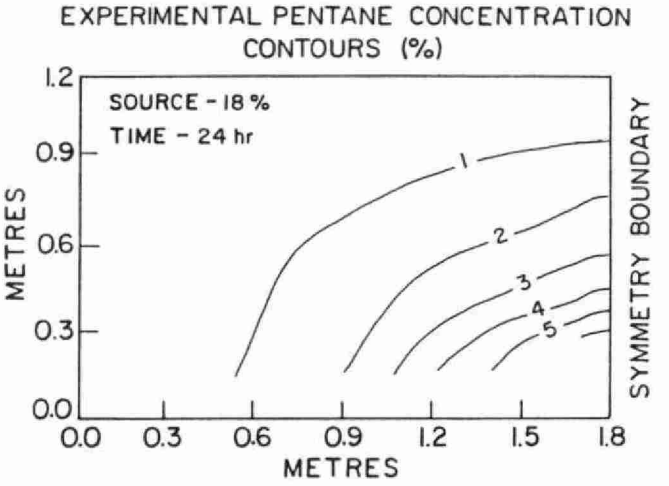


Figure 5



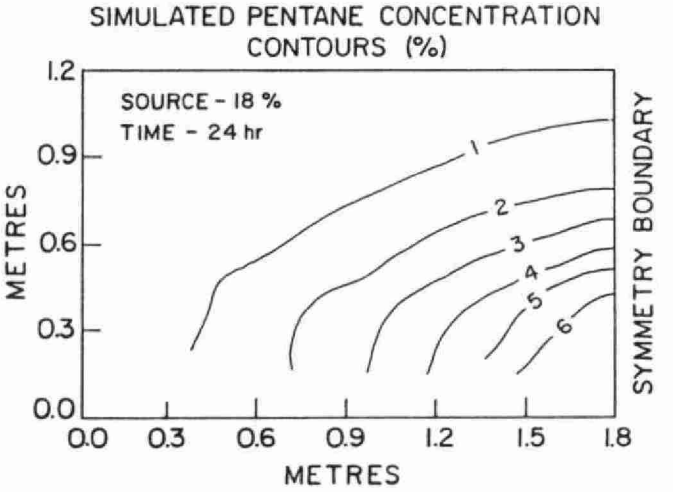


Figure 6

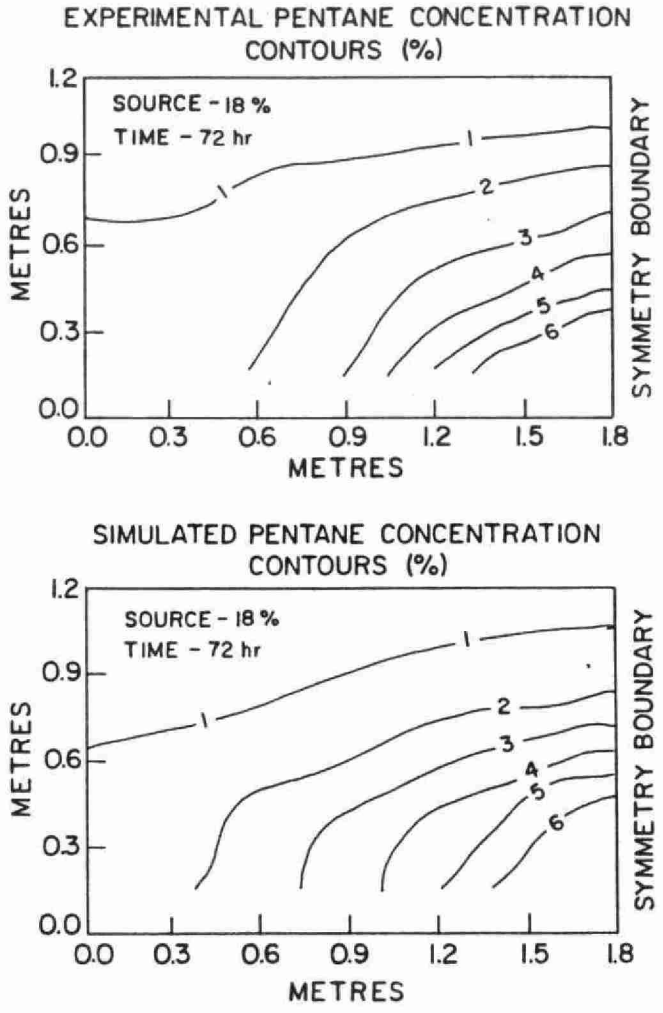


Figure 7

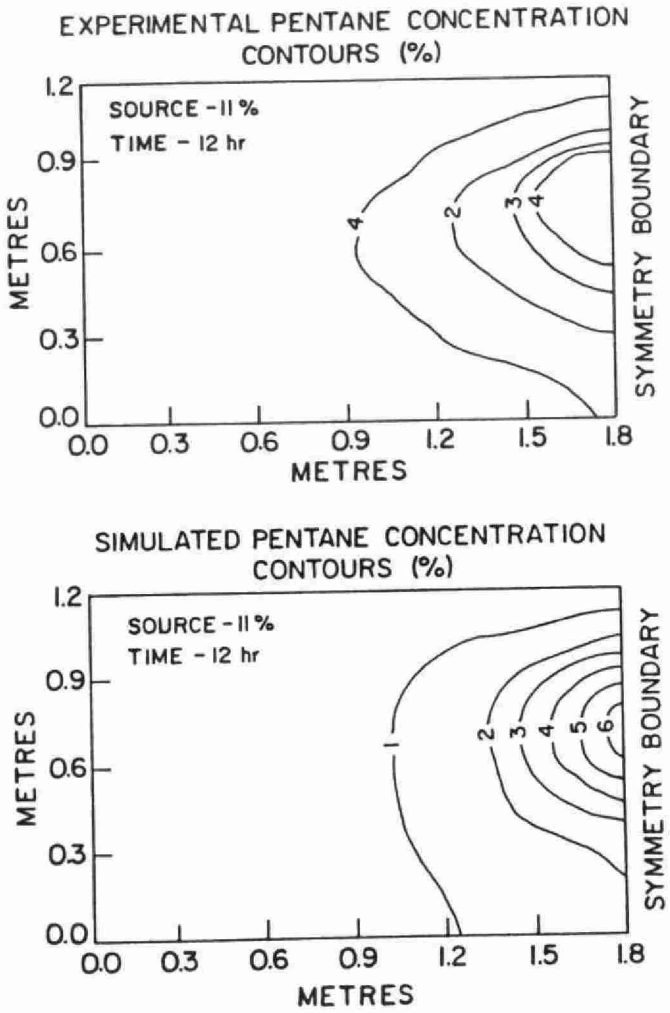


Figure 8

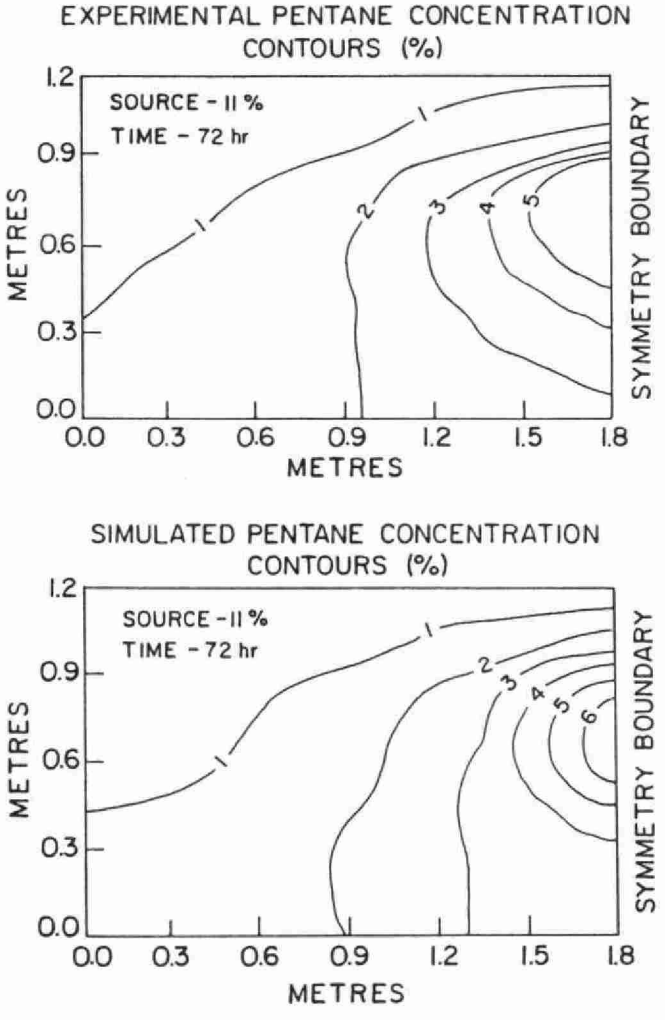


Figure 9

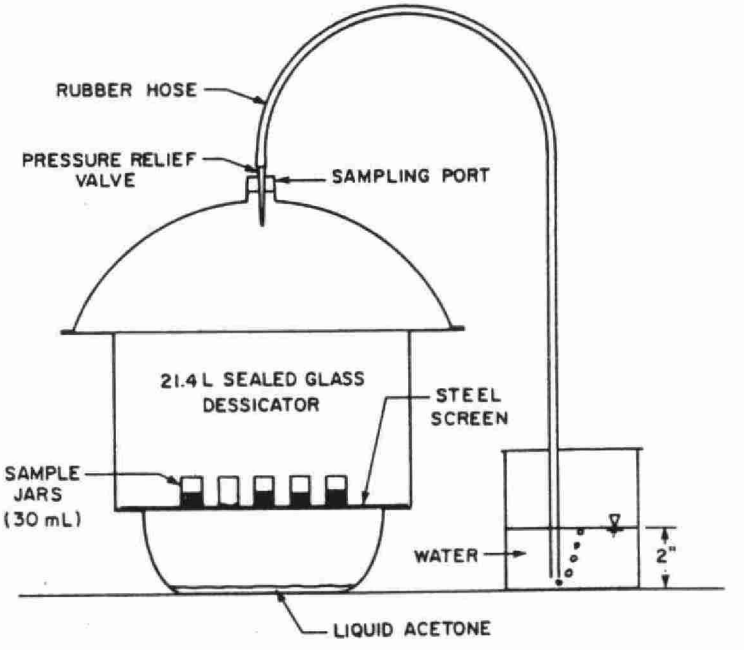


Figure 10

DETERMINATION OF FREUNDLICH CONSTANTS
FOR ACETONE ADSORBING ONTO TWO SOILS

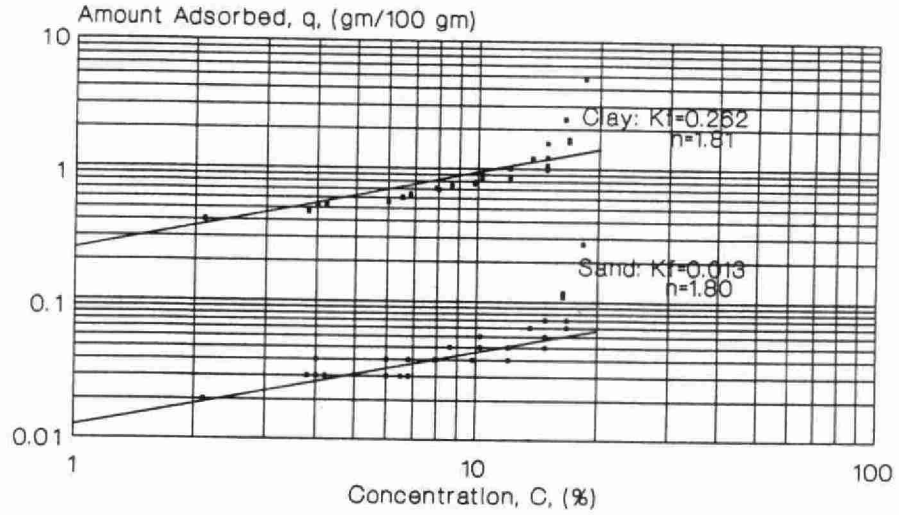


Figure 11

DETERMINATION OF FREUNDLICH CONSTANTS
FOR TCE ADSORBING ONTO CLAY

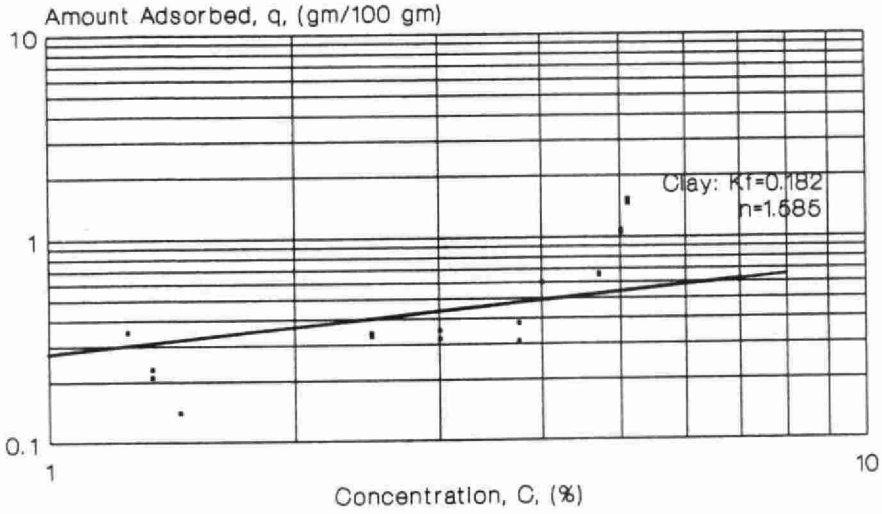
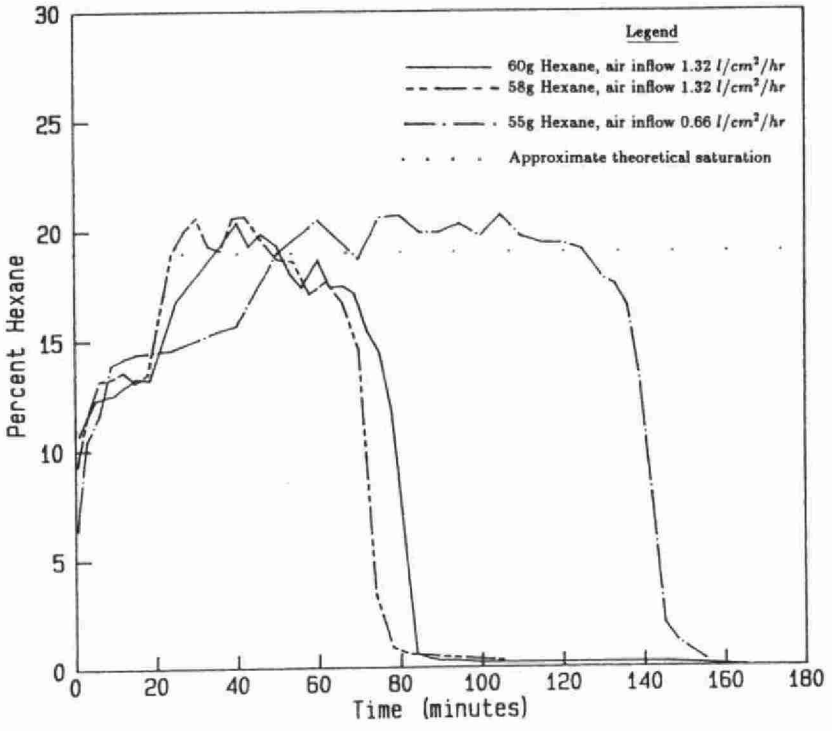
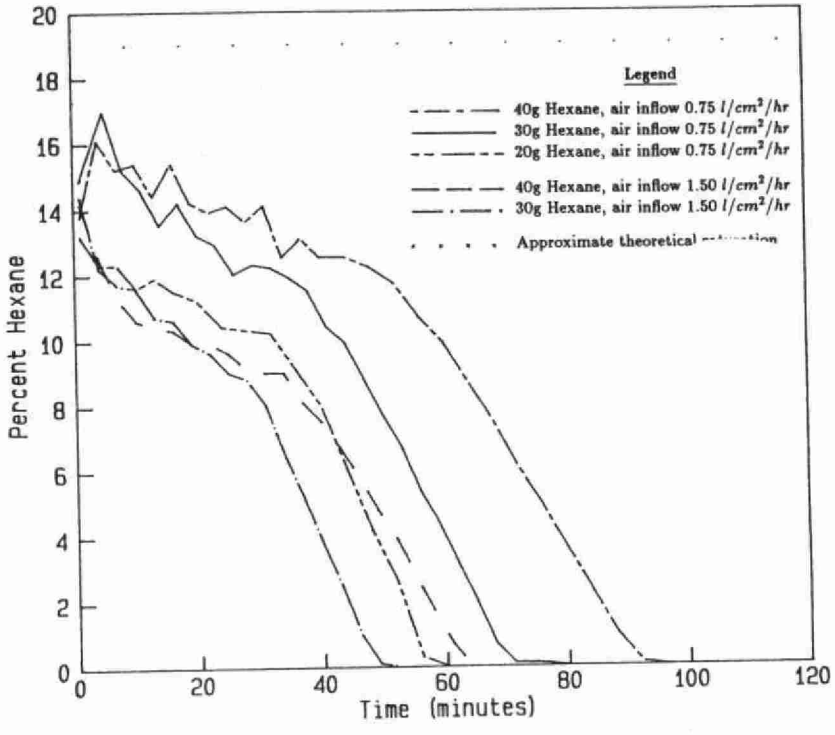


Figure 12



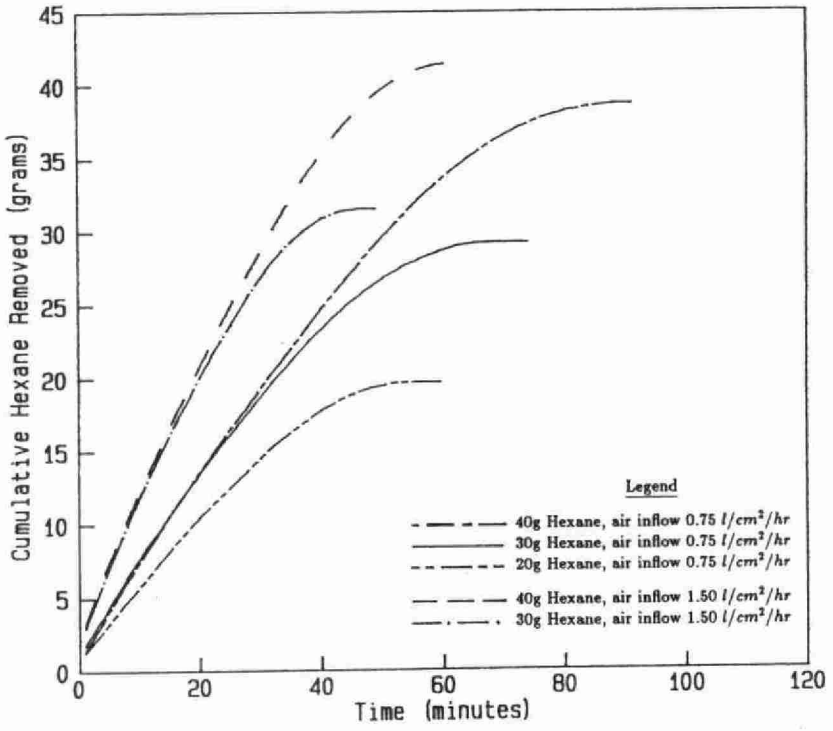
PERCENT HEXANE IN EXHAUST VAPOUR
(bottom portion of column at residual saturation)

Figure 13



PERCENT HEXANE IN EXHAUST VAPOUR
(5 cm diameter cylindrical plug)

Figure 14



CUMULATIVE HEXANE IN EXHAUST VAPOUR
(5 cm diameter cylindrical plug)

Figure 15

(7592)
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